

Research Laboratory  
of the  
Portland Cement Association

BULLETIN 9

Should Portland Cement Be  
Dispersed?

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FEBRUARY 1946

CHICAGO

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JOURNAL OF THE AMERICAN CONCRETE INSTITUTE  
New Center Building, 7400 Second Boulevard  
Detroit 2, Michigan  
*November 1945, PROCEEDINGS Vol. 42, p. 117*







JOURNAL  
of the  
AMERICAN CONCRETE INSTITUTE  
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Vol. 17 No. 2

7400 SECOND BOULEVARD, DETROIT 2, MICHIGAN

November 1945

## Should Portland Cement Be Dispersed?\*

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Member American Concrete Institute

### SYNOPSIS

A development of definitions of *wetting* and *dispersion* is followed by a discussion of dispersion of portland cement.

From elementary principles it appears that a wetting agent is unnecessary, for portland cement is highly hydrophilic.

The dispersed state of portland cement in water is defined as that state in which interparticle attraction in a fresh paste is absent or so weak that it has no appreciable effect on the physical properties of the fresh paste. Experiments and reasoning from general principles indicate that dispersion would be undesirable because it would increase the rate and amount of sedimentation and promote particle-size segregation in cement paste; it would destroy the plasticity of the pastes and give them the properties of a fluid, a probably undesirable change; it would have no beneficial effect on rate of hydration during the early stages through an increase in exposed surface area because the whole surface is normally exposed to water even when the particles are flocculated.

A reduction in interparticle attraction short of actual dispersion should reduce the water required for a given slump, but it would not improve workability except in unusually rich mixes. It would increase bleeding.

Air entrainment requires an increase in paste content and reduction of water content to maintain a given slump. It reduces strength but improves frost resistance. It improves workability and reduces bleeding.

Air entrainment together with some reduction in interparticle attraction affects paste content and water requirement in the same way as air entrainment alone, but the increase in paste content is smaller and the reduction in water content is greater than when there is no reduction in interparticle attraction. Air entrainment offsets the undesirable effects of reducing interparticle attraction on plasticity and reduces bleeding.

Some agents do not affect the chemical processes of hardening; their effects on strength can be predicted from the voids-cement ratio. Others tend to retard hydration unless they contain an accelerating agent. Such agents have different effects with different cements.

\*Received by the Institute March 19, 1945.

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### INTRODUCTION

This discussion was prepared in response to many requests for information on various admixtures sold as dispersing agents. The questions are usually one of two types: (1) What is the effect of Admixture X on concrete? and (2) What is back of the idea of dispersion of cement? This discussion will deal primarily with the question of what is back of the idea of dispersing cement—not with the actual merits of preparations that have been sold as dispersing agents.

Some materials sold as dispersing agents may have merit because of effects not related to dispersion. However, they cannot be endorsed on the basis of some of the claims made for them. In explaining results obtained or hoped for the assumptions have been made that a normal cement paste is composed of individual flocs (clusters) of cement grains such as may be seen when a small amount of cement is suspended in a large volume of water; also that water for hydration does not penetrate the flocs and hence that the cement cannot hydrate as well as it might; that the water that is “trapped” in the flocs does not contribute to workability. It is then further assumed that the flocs of cement grains can be caused to disintegrate, that is, that the grains in a floc can be dispersed, by adding a suitable agent which causes the grains to acquire electrostatic charges and thus to become mutually repellent; and that when the cement grains are thus dispersed they hydrate more rapidly and to a greater extent than when flocculated. Moreover, it is assumed that when the particles are brought to a state of mutual repellency, the amount of bleeding or “settlement-shrinkage” is reduced. Dispersion is said also to improve resistance to frost action.

Most of these assumptions seem plausible, but they are not compatible with the results of recent researches on the nature of cement paste and on the whole are believed to be untenable on either a theoretical or empirical basis. The basis for this conclusion will be given briefly in this discussion.

The question to be discussed can easily become confused by the fact that some preparations used as dispersing agents are actually mixtures containing not only a dispersing agent but also an accelerator such as calcium chloride, and by the fact that most, if not all, such materials cause more or less air-entrainment. Yet *all* the effects of such mixtures have been attributed, by some, to the supposed dispersion of the cement particles. It is therefore necessary to remember that what may be said in the following discussion against the idea of dispersion does not necessarily impugn any particular preparation unless the predominant effect of the preparation is that of dispersing the cement.

Owing to the manner in which various types of materials of this class have been introduced to the concrete industry, there is some confusion



with respect to the terms "wetting agent," "dispersing agent," and "air-entraining agent." Therefore, a secondary aim of this discussion is to clear away some of the confusion with respect to terminology. It is especially important to grasp the fact that certain difficulties surround the use of the term "dispersion" as applied to portland cement. To bring out the nature of these difficulties, it is necessary to present a brief discussion of fundamentals. This discussion leads to a definition of dispersion of portland cement paste on which the final part of the paper is based. The reader is asked to avoid applying the final conclusions concerning dispersion as defined here, to dispersion defined in some other way.

The discussion of fundamentals will be found rather sketchy. For those seeking fuller information a guide to the literature is provided.

### THE PHENOMENON OF WETTING\*

When a drop of liquid is placed on a clean surface of a solid, it may either spread on the surface or remain as a more or less flattened drop, showing a definite angle of contact with the surface. When the liquid spreads spontaneously, wetting is said to be complete (contact angle = zero) and, if the liquid is water, the solid is called hydrophilic. If water does not spread but establishes a finite contact angle, wetting is incomplete or partial and the solid is regarded as hydrophobic.<sup>1b</sup> Partial wetting, that is, the formation of a contact angle, denotes that the force of adhesion between the solid and the liquid (which tends to cause the liquid to spread over the surface) is less than the surface tension of the liquid, which tends to cause the liquid to gather itself into a drop. Conversely, wetting is always complete when the force of adhesion exceeds the surface tension of the liquid.

A wetting agent is usually a material composed of elongated organic molecules, the molecules having an affinity for the solid at one end and affinity for the liquid at the other. Such an agent forms a layer of molecules on the solid, the molecules being so oriented as to present a wettable surface to the liquid.

When the force of adhesion between a powdered solid and a liquid is less than the surface tension of the liquid, the powder and the liquid are difficult to mix unless a suitable wetting agent is used. Or if the adhesion tension exceeds the surface tension only slightly, a wetting agent will be noticeably helpful. On the other hand, if the solid and liquid show a strong mutual attraction, the liquid will spread over the solid surface without outside aid. For any given case the surface tension and adhesion tension may be measured and the need for a wetting agent

\*See Ref. 1 at end of paper.



judged from the results. It is simpler, however, merely to observe directly whether wetting is complete or not. For example, if the specific gravity of the solid exceeds that of the liquid, small particles of the solid, when scattered on the surface of the liquid, will sink readily if the contact angle is very small or zero, or they will remain on the surface if the contact angle is sufficiently large, as does an oiled needle on water. In the case of portland cement and water it is still simpler merely to observe the absorption when water is placed in a crater of dry cement; capillary absorption is readily apparent unless the cement contains a "water-repellent" substance.

Any such criteria applied to portland cement would show that the wetting of portland cement by water could hardly be improved by a wetting agent, unless the cement has acquired a "water-repellent" coating. The degree of solubility of the constituents of cement and, in fact, the rapid formation of hydrates that occurs immediately on contact with water show that portland cement has a strong affinity for water. The attraction is so strong that each cement grain becomes completely surrounded by water even though in a dilute suspension the grains are clustered. This is shown by the fact that during sedimentation of a concentrated suspension, i.e., during bleeding, the *whole* surface area of the cement is effective in regulating the rate of flow of water.<sup>2</sup> So far as the writer knows, no one has seriously contended that cement needs a wetting agent.

When a powder is readily wetted, so that each grain becomes surrounded with water, the grains are necessarily separated, at least by a thin film of water. Because of this, the wetting of a powder by immersion in a liquid is sometimes referred to as dispersion. However, it is advantageous and in line with modern textbook terminology to draw a distinction between wetting and dispersion. As described above, the term *wetting* pertains to the spontaneous spreading of a liquid over a surface. It applies to any shape of surface, not to particles alone. Dispersion, on the other hand, pertains only to particles.\* It is the opposite of flocculation, agglomeration, or coagulation. Wetted particles may be in either a flocculated or a dispersed state. Flocculated particles in a liquid may be held together by forces acting across separating films of liquid; hence, a flocculated state is not necessarily one requiring particle-to-particle contact.

These remarks give a general idea of what is meant by dispersion, flocculation, and wetting, but a definition of dispersion wholly adequate for the present discussion cannot be given without considering some additional details of the phenomenon.

\*But not necessarily to *solid* particles only.



### INTERPARTICLE FORCES

According to present-day theories, the interparticle force in an aggregation of particles in a fluid medium is made up principally of the following components:

(1) An ever-present force of attraction (van der Waal's forces) which causes adjacent particles to adhere; and

(2) An electrostatic force of repulsion that opposes the force of attraction. This repulsion is strongly dependent on the environment of the particles and is therefore subject to control.

The control of interparticle force may involve controlling the kind and concentration of electrolytes, or the use of certain kinds of organic molecules or colloids.

Because of the nature of the relationships between distance of separation and intensity of repulsion and intensity of attraction, two particles may have minimum potential energy when they are separated by a small but definite distance.<sup>3, 4</sup> Hence, even in the flocculated state, suspended particles may tend to remain slightly separated.\*

### DISPERSION

#### Spontaneous dispersion

Dispersion has been pictured as a spontaneous process whereby particles bearing like electrostatic charges "spring apart and stay apart" by distances easily observed with the microscope. However, even under the most favorable conditions, the forces of repulsion in a suspension are effective over only very short distances. Indeed, if the particles were separated only by the effective distance of repulsion, they would appear to be in contact under ordinary magnification. Nevertheless, if the particles are very small, they may be capable of dispersing themselves by their Brownian motion, far beyond the range of interparticle forces. Brownian motion is a haphazard movement, or vibration, caused by unbalanced impacts of the molecules of the surrounding medium. If a particle is small enough, the forces of the impacts received simultaneously from different directions do not balance and the particle thus acquires motion.

Particles having Brownian motion wander at random and tend to bounce away from each other when they collide. If the forces tending to keep the particles in motion exceed the force of attraction between the particles, then a state of dispersion will spontaneously be maintained. On the other hand, if the forces of attraction between the particles exceed the forces tending to keep the particles in motion, then a state of flocculation, or agglomeration, will persist. Note that interparticle

\*For a thorough discussion of interparticle forces, see Ref. 5.



repulsion is not necessary for dispersion; but, of course, the more the interparticle attraction is cancelled by interparticle repulsion, the smaller the amount of kinetic energy required to keep the particles dispersed.

Brownian motion can occur to a significant degree only among very small particles—colloidal particles. Hence, portland cement cannot be caused to disperse spontaneously, for cement particles are predominantly microscopic, not colloidal.<sup>6</sup>

#### Mechanical dispersion

Even when spontaneous dispersion is not possible, dispersion can be effected mechanically. Stirring a suspension tends to separate the particles, particularly if the stirring is violent. The degree to which the particles will become separated on stirring depends largely on the intensity of the interparticle attraction. Of course, mutually repellent particles should be more easily dispersed than those which have some tendency to stick together.

\* \* \*

The discussion immediately above was presented to show that some of the phenomena pictured in connection with the use of dispersing agents with portland cement actually can occur only among particles that are of truly colloidal dimensions. It must be added that whether or not spontaneous dispersion takes place is of little practical consequence. *The important question is whether it is necessary or desirable to cancel or reduce the forces of interparticle attraction that normally predominate over the forces of repulsion in a suspension of cement particles in water.*

### INTERPARTICLE ATTRACTION AND PASTE PROPERTIES

Although the influence of interparticle attraction on the physical properties of pastes will be discussed more fully in the following section, two important effects may be mentioned at this point. The first is that the greater the interparticle attraction, the stiffer will a paste seem to be when it is stirred. In comparatively concentrated suspensions such as cement pastes, where interparticle attraction predominates over repulsion, the suspension behaves more like a solid than a fluid.<sup>7a, 7b\*</sup> The other effect appears when suspensions are allowed to settle. If the forces of attraction predominate, the large and small particles settle together. If the forces of repulsion predominate or if the net force of attraction is very weak, particles that would remain in contact when quiescent become separated as they fall through the liquid during sedimentation.

The cause of this may be seen by considering two particles of different size adhering to one another at the beginning of their fall through the

\*It behaves like a solid in that it is capable of withstanding small shearing forces. See page 129, "Effect of Flocculation on Plasticity."



liquid. The drag of the liquid on the small particle will be greater per unit mass than that on the large one; therefore, a force tending to separate them will develop. If this force, which depends upon the difference in the size of the particles, exceeds the force of attraction, the particles will separate, the larger particles falling more rapidly. When the attractive forces are very weak, and especially when the particles are mutually repellent, the sediment that is formed tends to be non-uniform in composition, the proportion of coarse particles increasing toward the bottom of the sediment. Moreover, the sediment formed is compact and difficult to redisperse, whereas a flocculated sediment is bulky, soft, and easily restored to its original state in the suspension. This feature of the behavior of the dispersed suspension is very significant with respect to the question of dispersing cement, as will be developed below.

#### DEFINITION OF DISPERSION APPLICABLE TO CEMENT PASTE

The foregoing discussions serve to show that a criterion for dispersion applicable to colloidal suspensions is not altogether applicable to temporary suspensions of non-colloidal particles; dispersion cannot mean exactly the same thing for both types of suspension. Yet circumstances seem to require using the same term for both cases; indeed, there is considerable justification for it. The dilemma is avoided by thinking in terms of interparticle attraction instead of the repulsion that is implied by the word "dispersion." A suitable definition of dispersion can be set up in terms of the influence that interparticle attraction has on certain properties of suspensions, particularly, the force-flow relationship. When interparticle attraction is absent or negligible, a suspension that is not too concentrated flows like a true fluid; but when interparticle attraction is not negligible, the suspension acquires the properties of a plastic solid to some degree. Also, in a *dilute* suspension of particles, segregation of sizes takes place during sedimentation if the interparticle attraction is absent or weak and it does not take place if interparticle attraction is strong. In view of such observations as these the following definition of dispersion is used in the discussion of cement paste that follows:

*When interparticle attraction in a fresh cement paste is so weak that it has no appreciable effect on the behavior and physical properties of the paste, the particles in the paste may be said to be dispersed.*

By this definition we would call any suspension dispersed in which the interparticle attraction is zero or negative. This would not disagree with other definitions applied to colloidal suspensions. But we would also call a suspension dispersed if the interparticle force was positive, but too weak to have an appreciable effect on the physical properties of



the suspension. It should be noted that the definition does not rest on the presence or absence of particle-clusters; neither does it imply that dispersion is a spontaneous process.

This definition admits the possibility of various degrees of interparticle attraction among the particles in flocculated suspensions, that is, suspensions in which the attraction has an effect on flow-properties, etc. Consequently, we can discuss two questions, one pertaining to the desirability of producing dispersion, and one pertaining to the desirability of changing the intensity of interparticle attraction in a flocculated paste.

### DISPERSION OF PORTLAND CEMENT

#### Flocculated state of normal portland cement paste

As implied at various points in the foregoing discussion, there is no question but that cement particles in a normal paste are flocculated. This may be seen by microscopic examination of cement-water mixtures sufficiently dilute to transmit light or by observation, at low magnification, of the texture of pastes through the wall of a glass container.

The process by which cement becomes flocculated may be visualized as follows: Under the action of a mechanical mixer, cement particles probably tend to be dispersed during the first few seconds of contact with the water. Chemical reactions begin immediately and continue at a relatively high rate for a period of not over five minutes—probably less than two minutes—during which time the electrolyte concentration in the mixing water increases rapidly. The electrolytes (apparently the hydroxyl ions) bring about flocculation of the cement particles.

During the same period a coating of hydrates forms on the cement grains. Once this coating has formed, and the electrolyte solution has reached full strength, the rate of reaction becomes very low and thus the cement remains comparatively dormant chemically. This state lasts for a considerable period, usually about an hour. The paste remains plastic during this period, and, if left undisturbed, undergoes sedimentation ("bleeding").

### EFFECT OF FLOCCULATION ON AMOUNT OF SETTLEMENT

Except for certain features that need not be discussed here, the sedimentation of cement pastes has been shown to be essentially like that of other concentrated suspensions of flocculated mineral powders. Various experiments have been carried out that reveal the effect of flocculation on this process. Steinour<sup>2b</sup> observed the sedimentation of emery particles both flocculated and not flocculated. Typical results are given in Table 1:



TABLE 1

| Material | Diameter,<br>microns | Fluid<br>Content, % | Amount of Final Settlement,<br>% of original height |             |
|----------|----------------------|---------------------|-----------------------------------------------------|-------------|
|          |                      |                     | Dispersed                                           | Flocculated |
| Emery A  | 12.2                 | 65                  | 36                                                  | 17          |
| A        | 12.2                 | 80                  | 63                                                  | 44          |
| B        | 9.6                  | 75                  | 55                                                  | 35          |

As shown in the last two columns of the table, flocculation *reduced* the amount of settlement at all concentrations.

The amount of settlement is influenced by the concentration of the flocculating agent. This is deduced from data such as the following obtained by the writer.<sup>8</sup>

TABLE 2—SEDIMENTATION OF PULVERIZED SILICA IN LIME-WATER  
(60 ml of solution per 100g of silica)

| Initial Concentration of $\text{Ca}(\text{OH})_2$<br>in Mixing Water | Rate of<br>Settlement<br>cm/sec x $10^6$ | Final Settlement<br>per Unit of Original<br>Height, % |
|----------------------------------------------------------------------|------------------------------------------|-------------------------------------------------------|
| $\frac{1}{4}$ saturated solution                                     | 58                                       | 10                                                    |
| $\frac{1}{2}$ saturated solution                                     | 53                                       | 5                                                     |
| saturated solution                                                   | 53                                       | 1                                                     |

Steinour<sup>9</sup> in tests on another silica-powder observed similar but less pronounced effects, the settlement being 12 and 19 per cent for saturated and  $\frac{1}{6}$ -saturated solutions, respectively, with the initial fluid content at 60 per cent.

Results of some experiments with portland cement are given in Fig. 1. This shows the volumes of sediment formed from dilute suspensions (initial fluid-content 86 per cent by volume) of cement in various mixtures of ethyl-alcohol (denatured) and water, ranging from all water to all alcohol. One point represents the results obtained in pure toluene.

The addition of alcohol up to about 50 per cent by volume increased the sedimentation-volume;\* higher concentrations of alcohol reduced the volume, finally to a point below that for water alone. All suspensions were flocculated to the extent that no separation of particle sizes could be observed, except the one in straight alcohol. In the latter, most of the cement settled out quickly, the largest particles concentrating toward the bottom of the sediment while the very finest flour remained in suspension, even after 24 hours, probably because of Brownian motion.

\*Defined as the ratio of bulk volume of the sediment to the solid volume of the particles.



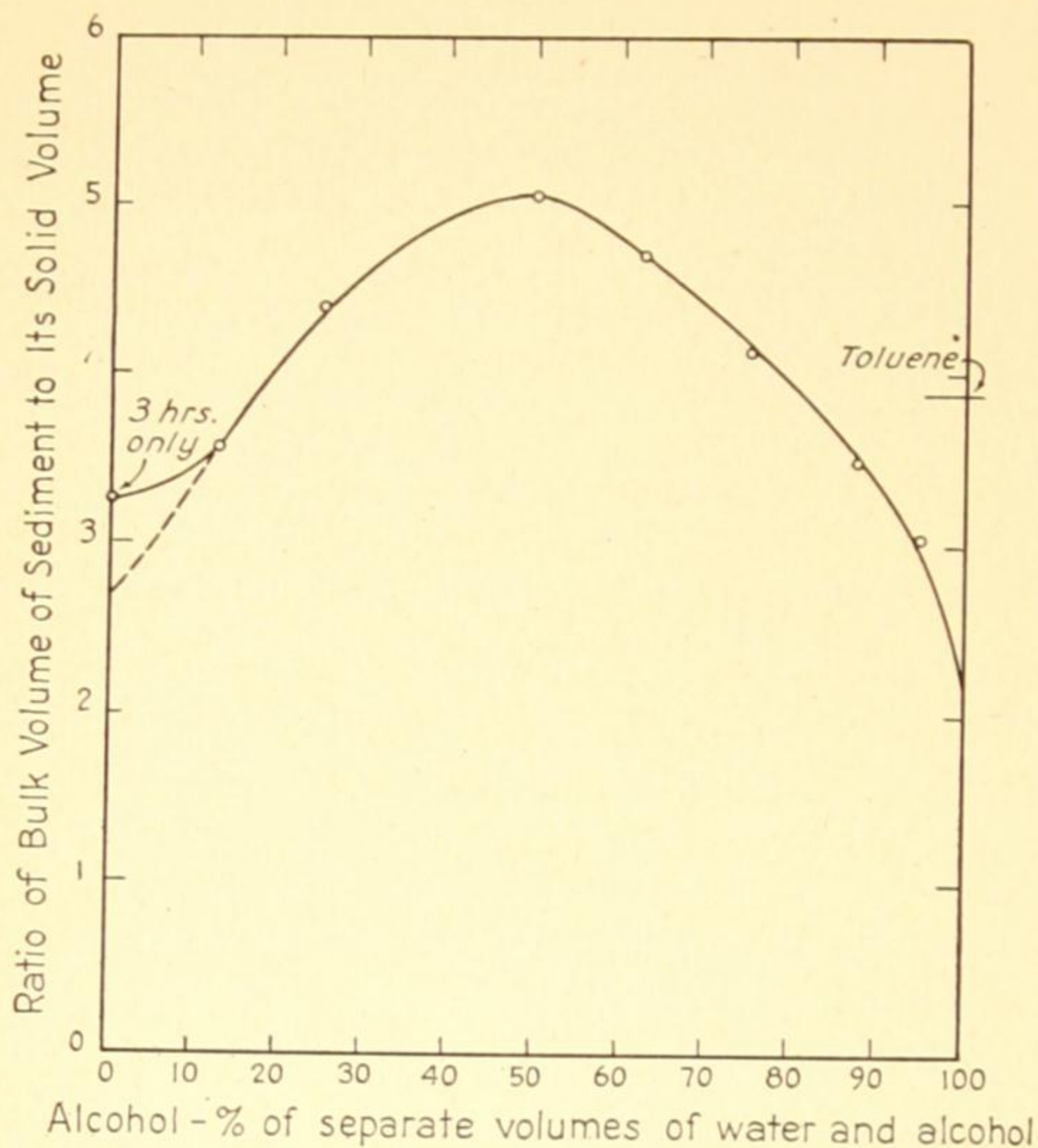


Fig. 1—Sedimentation volumes of cement in alcohol-water solutions and in pure toluene. — Period of settlement 24 hours, except as noted.

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It is reasoned that in settling from dilute suspensions the particle-flocs, in making contact with the sediment, tend to form arches or bridges enclosing relatively large spaces which contribute to the bulkiness of the sediment.<sup>10, 11</sup> The greater the extent to which such arches are able to withstand the pull of gravity, the greater will be the final volume of the sediment. It seems reasonable to assume that the greater the interparticle attraction the greater the strength of the arches and the bulk of the sediment. Therefore, the factors that control interparticle attraction should control sedimentation volume.

The reversal in the slope of the curve of Fig. 1 can be accounted for as follows:\* The interparticle force in any given suspension is determined by the kind and concentration of substances in solution and by the force of adhesion between the particles and the liquid medium. Electrolytes in solution or certain types of organic molecules tend to make the particles electrostatically repellent. (Under most circumstances the electrostatic repulsion is at a maximum at very low electrolyte concentrations.) Also, the adhesion of the liquid to the surface and the adsorption of ions or molecules from the solution by the surface tend to cancel some of the particles' surface energy, the surface energy being the source of the force of attraction between the particles. When alcohol is added, it apparently reduces the force of adhesion† between the water and the cement particles

\*This explanation is necessarily speculative, since specific data on interparticle forces in this system are lacking. Other explanations can be devised.

†This is directly indicated by the fact that the higher the alcohol content, the lower the dielectric constant of the solution. See Ref. 4.



and thus increases the net force of attraction. At the same time, the addition of alcohol decreases the solubility of the cement constituents and thus favors an increase in electrostatic repulsion, a change tending to offset the effect of the decrease in the force of adhesion between liquid and solid. Evidently, from Fig. 1, one effect is predominant at low alcohol concentration and the other effect is predominant at high concentration.

These data demonstrate that the forces of interparticle attraction in cement-water paste are not as high as they might be and that if a change in the force of flocculation is desired, it could be either an increase or a decrease, according to choice.

Tests with various dispersing agents for portland cement show that they produce a condition similar to that found with cement alone in pure alcohol, but only in very dilute suspensions. Used in concretes or pastes in proportions recommended for field use, they do not cause such dispersion; the pastes clearly show the effects of interparticle attraction. There is evidence, however, that these agents weaken the forces of attraction.

#### Effect of flocculation on rate of sedimentation

The effect of flocculation on the rate of sedimentation is illustrated in Fig. 2. The curve illustrates the following general rule:

In *dilute* suspensions, flocculation increases the rate of sedimentation over the average for the dispersed material; in *concentrated* suspensions flocculation *decreases* the rate.

Portland cement pastes as used in practice may be classed as concentrated suspensions; accordingly, *they settle (bleed) more slowly than they would if the particles were dispersed.*

At high dilution, flocculation increases the rate of sedimentation because the displaced water is able to flow mostly around the flocs, each floc acting much like a single large particle. But at some sufficiently high particle-concentration the particles form a floc-structure so continuous that the displaced water can flow only through the floc-structure itself. In an intermediate range, the flow is partly around and partly through the flocs, a condition giving rise to "channeled bleeding."<sup>13</sup>

The actual conditions in a normal cement paste seem to be about as follows: From considerations already discussed, it seems that before or during the process of flocculation the cement particles become coated with hydrates and the coating acquires a layer of adsorbed water and ions. The particles are so concentrated that when flocculation occurs *they do not draw together into discrete groups* but they form a continuous network. The bonds of the network are, it would be imagined, at points



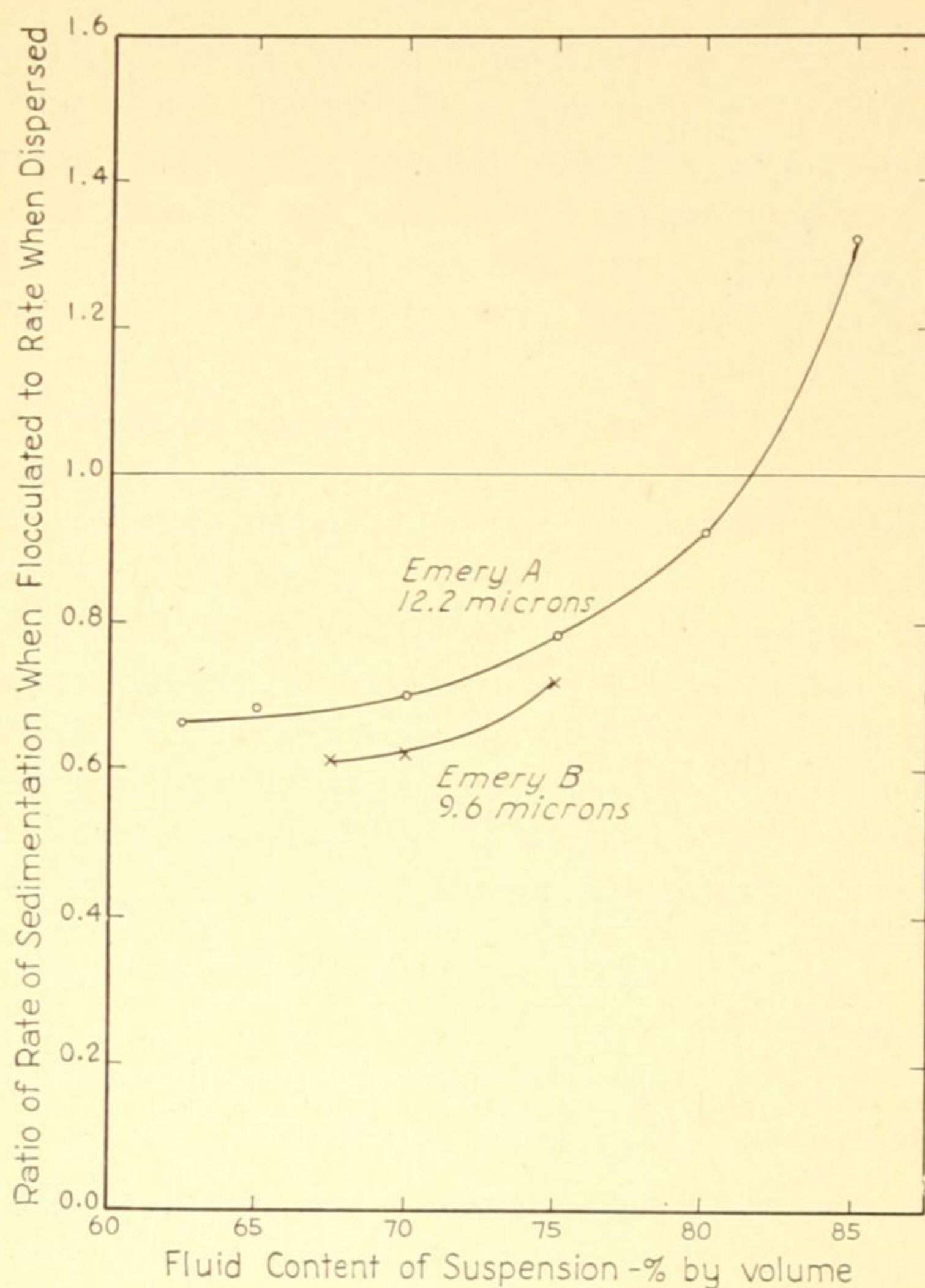


Fig. 2—Effect of flocculation on rate of settlement as influenced by concentration of solids.

(From Ref. 2b)

on adjacent particles that would be in contact were it not for the strongly attached adsorbed layer.

This conclusion is required by at least three conditions:

(1) The nature of the relationship between changes in water content and corresponding changes in the rate of bleeding is such as to show that a change in water content causes a change in the spacing of the network; that is, the effect is *not* that of changing the spacing between clusters of particles.

(2) Steinour's experiments showed that the viscous resistance to sedimentation involves the same amount of particle surface when the particles are flocculated as when they are not flocculated.

(3) Measurements of hydrostatic pressure in cement pastes showed that the particles in a fresh paste are supported entirely by the liquid; that is, none of their weight is transmitted to the bottom of the vessel through point-to-point contacts.

Points (1) and (2) show that the particles cannot exist as separate flocs. Point (3), supported by (1), shows that the particles are normally surrounded with water.



Thus, the evidence is so strong as to be little short of proof that a cement paste is to be regarded as a continuous network of particles in water, the bonds of the network being the forces of flocculation acting across small distances at points of near-contact. In other words, a cement paste may be considered as one large floc; hence, all the water in the paste is within the floc.

So far as the effects of bleeding are concerned the results obtained when the particles are subject to the force of flocculation are clearly preferable to what they are when the particles are free from that force. This becomes doubly evident when it is recalled that during the bleeding of concrete the aggregate soon forms a static framework within the cells of which the paste continues to settle. Even with a normally flocculated paste the settlement is enough to weaken the bond with the under-surfaces of the aggregate particles. Dispersion would not only increase this effect but also would tend to destroy the uniformity of the hardened paste by promoting stratification, as has already been pointed out. If cement pastes were not normally flocculated, it would seem advisable to add a flocculating agent.

From the facts just reviewed it is plain that any claim that *dispersion* is a means of reducing bleeding or "shrinkage before hardening" is based on knowledge of the effect of dispersion on the settlement of *dilute* suspensions and not of the effect on pastes. Also, any deductions based on the assumption that the cement particles in a normal paste exist in discrete flocs from within which water for hydration is excluded are bound to lead to erroneous conclusions, for the evidence is overwhelming that no such condition exists.

#### **Effect of flocculation on plasticity**

Flocculation is essential to the plasticity of granular suspensions. When the particles are not flocculated, the mixture behaves like a fluid; it flows under any force, however small, and it can have only the cohesiveness of the liquid itself. When the particles are flocculated, but the dilution is such that individual flocs exist, the mixture probably partakes both of fluidity and plasticity—plasticity increasing with increase in particle concentration. In normal cement pastes, the particles are so concentrated that the behavior of the paste is almost wholly that of a solid; in fact, it meets the definition of a gel, except that it is not colloidal. Under small stresses of short duration it responds both elastically and plastically, by far the greater part of the deformation being plastic.<sup>7</sup> This is true even of pastes thin enough to be poured.

When the strain produced by a sufficiently large force exceeds a limit, the material fails in shear, either with or without dilation, depending on the size and concentration of the particles. Thus when a paste (or a



concrete) is forced through a pipe, the deformation is laminar at first (as it is in fluid flow) until a limiting strain is reached, whereupon the material fails in shear at the pipe-wall, the flow from then on being "plug-flow."<sup>13</sup> With dilute pastes, plug-flow can be converted to viscous flow by producing high rates of flow. With concentrated pastes (or concretes) continuous viscous flow cannot be produced because of dilation due to particle interference.

The fact that a normal paste meets the definition of a solid, even exhibiting some elasticity, seems at first to constitute an anomaly, for already it has been shown that the particles are not in direct contact with each other. However, these facts, put together, only support the conclusion that interparticle attractions are effective across intervening layers of water. It seems self-evident that the cohesiveness, or stickiness, of the paste arises largely from these interparticle forces that give the paste its rigidity.

In contrast to the behavior just described, silica in water, cement in alcohol, or any other suspension in which the particles are not at all flocculated—such mixtures act like fluids; they may be mobile, but they are not plastic, and in the absence of entrained air have only the cohesiveness of the suspending medium. Thus, the question as to whether dispersion would be advantageous raises the question as to whether a fluid paste would be preferable to a plastic one.

It has not been demonstrated that concrete made with a *fluid* paste is more workable than one made with a *plastic* paste. On the face of it, the plastic paste would seem much to be preferred. This is indicated by the undesirable results obtained when pulverized silica, in the absence of a flocculating material such as lime, is used instead of cement. It is indicated also, and very strongly, by the nature of the sediment formed from dispersed suspensions. As said before, the dispersed suspension tends to stratify, but in concrete this is probably less serious than the fact that the sediment formed is very compact and rigid, difficult to redisperse, in contrast to a flocculated sediment which may be only a little less plastic than the original suspension. It is plain that during any delay in transportation or placing, a dispersed paste would exhibit very undesirable characteristics.

#### EFFECT OF WEAKENING INTERPARTICLE ATTRACTION

The discussion up to this point has dealt mostly with comparisons of the dispersed and flocculated states with respect to the properties of fresh concrete. There remains to be considered the effect of varying the interparticle attraction without producing a state of dispersion.



To interpret the test data that will be presented, we need first to observe that, with given materials, the consistency of fresh concrete depends on two factors:

- (1) The quantity of paste
- (2) The consistency of the paste

With respect to the properties of fresh concrete, entrained air is considered to be a part of the paste.

Among the materials sold as dispersing agents that we have tested, all changed both the quantity and consistency of the paste in a given mix. One material apparently softened the paste but had little effect on paste volume.\* Among those agents that influenced both volume and consistency of paste, all caused air entrainment and some apparently reduced interparticle attraction as did the one that had no effect on paste volume. None of these materials when used in concrete in recommended quantities produced dispersion as defined above. That is, they all left the pastes in the flocculated state, but some of them seemed to reduce the intensity of interparticle attraction. (The statements as to interparticle attraction are made tentative because the evidence concerning interparticle attraction is not quantitative, and is somewhat indirect.) The effects of these different types of agents on the composition and properties of fresh concrete will now be discussed.

#### **Effect of an agent that reduces interparticle attraction without entraining air**

The influence of interparticle attraction (force of flocculation) on paste consistency is well illustrated by the effect of oleic acid on a mixture of cement and kerosene. When a paste of cement and kerosene is made, we find that interparticle attraction is so strong that the cement particles form a relatively rigid structure, capable of supporting a small weight. Addition of a very small amount of oleic acid during mixing will produce a noticeable change in appearance and a softening of the paste. This change continues as the dispersing agent is added drop by drop, with constant stirring, the paste becoming much like cement-water paste in consistency and texture. In this state it will bleed like cement paste and have similar plasticity. Finally, a single, last drop of oleic acid (in about 500 cc of paste) will cancel interparticle attraction, i.e., it will produce a state of dispersion.

Thus, we see that varying the concentration of a dispersing agent will change the consistency, cohesiveness and bleeding characteristics of a paste even though actual dispersion is not produced.

The effect of the one agent mentioned above that apparently reduced interparticle attraction without entraining air, here called Agent A, is

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\*This material is not sold as a dispersing agent. Nevertheless, tests show that when used in sufficient amount, it reduces interparticle attraction.



shown in Table 3. These results indicate that when this agent was present, slightly less paste was required for a given slump.\* As a matter of fact, this is the only evidence at hand, other than observations of the behavior of very dilute suspensions, that the interparticle attraction was reduced. We reason that since the average aggregate-particle spacing was less when the agent was present, and since the slump was the same, the paste containing the agent must have been softer. This reasoning arises directly from the observation that the higher the water-cement ratio of the paste, and hence the softer the paste, the less paste required for a given slump.

**TABLE 3—INFLUENCE OF AN AGENT WHICH REDUCES INTERPARTICLE ATTRACTION WITHOUT CAUSING AIR ENTRAINMENT—AGENT A**

| Ref.<br>No.<br>Series<br>305 | Agent<br>% Cem't<br>wt. | Cement<br>Content<br>sks/yd <sup>3</sup> | Slump<br>in. | Absolute Volume Composition of Concrete |        |       |      |                |
|------------------------------|-------------------------|------------------------------------------|--------------|-----------------------------------------|--------|-------|------|----------------|
|                              |                         |                                          |              | Aggreg.                                 | Cement | Water | Air  | Water<br>+ Air |
| 5                            | 0                       | 4.99                                     | 6.6          | .748                                    | .088   | .150  | .014 | .164           |
| 53                           | 1                       | 4.87                                     | 5.6          | .756                                    | .086   | .139  | .019 | .158           |
| 55                           | 2                       | 4.98                                     | 5.9          | .762                                    | .088   | .138  | .013 | .151           |
| *                            | 0                       | 4.99                                     | 5.6*         | .752                                    | .088   | .146  | .014 | .160           |
| 2                            | 0                       | 6.00                                     | 2.2          | .738                                    | .106   | .138  | .018 | .156           |
| 54                           | 1                       | 5.98                                     | 3.0          | .740                                    | .106   | .136  | .018 | .154           |
| 56                           | 2                       | 5.94                                     | 3.5          | .744                                    | .105   | .134  | .017 | .151           |
| *                            | 0                       | 6.00                                     | 3.2*         | .734                                    | .106   | .142  | .018 | .160           |

\*The figures in this line are estimated from Ref. 5 (or 2) on the basis of a 3 per cent change in water content for a 1-in. change in slump.

From the data in Table 3 it may be deduced that when using this particular agent with these materials, a given water-cement ratio can be obtained with about 5 per cent less cement than the amount required when not using the agent.

From the mere fact that Agent A reduced the water requirement for a given slump, we cannot conclude that workability and other properties were benefited. The net effect of using the agent was to replace a given paste with a smaller quantity of a softer paste. To conclude that this constitutes an improvement in workability would require also the conclusion that lean mixes are more workable than richer ones at the same slump, whereas the fact is that richer mixes are preferable under most conditions because of their greater cohesiveness, greater capacity for plastic deformation,<sup>†</sup> and greater ability to keep the aggregate from settling while the fresh concrete is in transit. A softening of the paste by reducing interparticle attraction would, in concrete of a given slump, give

\*With respect to plasticity, air is considered to be part of the paste as it obviously influences the average spacing of the aggregate particles.

<sup>†</sup>See Ref. 7b.



relatively less of the desirable characteristics just mentioned. Except in very rich mixes where the paste volume is higher than is necessary for satisfactory workability, the general desire seems to be to enhance these properties by stiffening the paste and increasing its volume. Such is the effect of adding mineral powders or increasing the cement content.

In this connection it may be recalled that a cement of high specific surface makes a stiffer, more cohesive paste than does a coarser one at the same water-cement ratio. Yet experience shows that only in very rich mixes is it necessary to use more water (or more paste) when a cement of high specific surface is substituted for a coarser one. This indicates that under some circumstances a stiffening, rather than a softening, of the paste is advantageous. An extreme example of this was reported by Kennedy.<sup>14</sup> He found that although no amount of water would make a sand-and-gravel mixture plastic, air entrained in the mixing water with a suitable agent made the mix appear as if it had been made with cement paste. As will be shown below, entrained air has a stiffening effect.

In general, it seems that increasing the stiffness of the paste, that is, giving it more "body," appears to be advantageous under ordinary conditions in mixes containing less than about  $5\frac{1}{2}$  sacks of cement per cu. yd. ( $1\frac{1}{2}$ -in. maximum size aggregate) or, in other terms, it appears advantageous if w/c exceeds about 0.5 by weight.

The lack of benefit from weakening the force of flocculation is probably due to the fact that the cement particles are normally not very strongly flocculated. This was pointed out before in connection with Fig. 1. It seems likely that if cement in water were flocculated as strongly as is cement in kerosene, a reduction in interparticle attraction might be beneficial under most, if not all, circumstances. But, in view of the relative weakness of the flocculating forces in cement-water paste, the value of further reductions in interparticle attraction is debatable.

This point may be emphasized by considering again the effect of reducing interparticle attraction on bleeding characteristics. The effect is to *increase* the amount of settlement (bleeding). However, the *rate* of settlement is affected very little. (See Table 2). The fact that the rate of settlement is affected very little shows that the *initial* texture of the paste is virtually unaffected by reducing the intensity of interparticle attraction. However, the *final* texture, after settlement, would be affected, the pastes having the lowest interparticle attraction forming the densest sediment. This might be advantageous were it not for the fact that any increase in the amount of paste settlement is accompanied by an increase in the depth of the under-aggregate fissures, which fissures weaken the concrete and make it more permeable. To be considered also is the probability that weakening the force of interparticle attraction



increases the tendency toward channeled bleeding with its attendant undesirable "sand boils"\* and it decreases the ability of the paste to hold the concrete in a plastic state while the concrete is standing or in transit. All effects considered, it seems very doubtful that a weakening of the force of flocculation improves the properties of fresh concrete, even though the slump may thereby be increased, except perhaps in mixes unusually rich in cement.

**Effect of an air-entraining agent having little or no effect on interparticle attraction—Agent B**

The use of some agents causes a pronounced increase in the air content of cement paste or concrete without appreciable effect on interparticle attraction. The manner in which this is brought about may be explained in simplified version as follows:<sup>15</sup> Any mechanical process that mixes a liquid with a gas tends to form a foam, although the foam may be scant and its life extremely short. If an agent is added that lowers the surface tension of the liquid (a "capillary-active" material), a foam forms more easily and it usually lasts longer than it does without the agent, especially if the agent, by reason of its adsorption at the air-liquid interface, enables the films to withstand shocks. Many organic compounds have this effect when used with water, the soaps being perhaps the most common class. A molecule of soap is relatively large, of the long-chain variety, having a hydrophilic "head" and a hydrophobic "tail." Such molecules tend to collect at the boundary between water and air (or water and oil) and, according to theory, array themselves in such a way that the hydrophilic part remains in the water and the less wettable (hydrophobic) remains in the air. These molecules thus create a boundary film which lowers the surface tension of the water and stabilizes any foam that is formed by mechanical action.

When such materials are used with portland cement paste, the entrained air is probably not to be regarded as a foam, strictly speaking. But the individual bubbles scattered through the paste are no doubt stabilized by the same mechanism that stabilizes the foam; therefore, it is appropriate to speak of such materials as foam stabilizers or air-entraining agents.

Fig. 3 and 4 show the effect of an air-entraining agent. In each diagram the lower line shows how the amount of water decreases as the air content increases. The upper line represents the sum of the volumes of air and water. Since all the mixes represented in a given diagram had the same cement content, the rise of the upper line represents the increase in paste content and the corresponding decrease in aggregate

\*In normal bleeding, water flows to the surface uniformly through all the interparticle spaces. In "channeled" bleeding, some of the flow occurs through randomly spaced channels which are the result of ruptures in the normally continuous "mesh" of the flocculated paste (see Ref. 12). The probability of the occurrence of such ruptures increases as the floc-structure is weakened by dilution. Presumably, the probability would be increased also by weakening interparticle attraction by means of a dispersing agent.



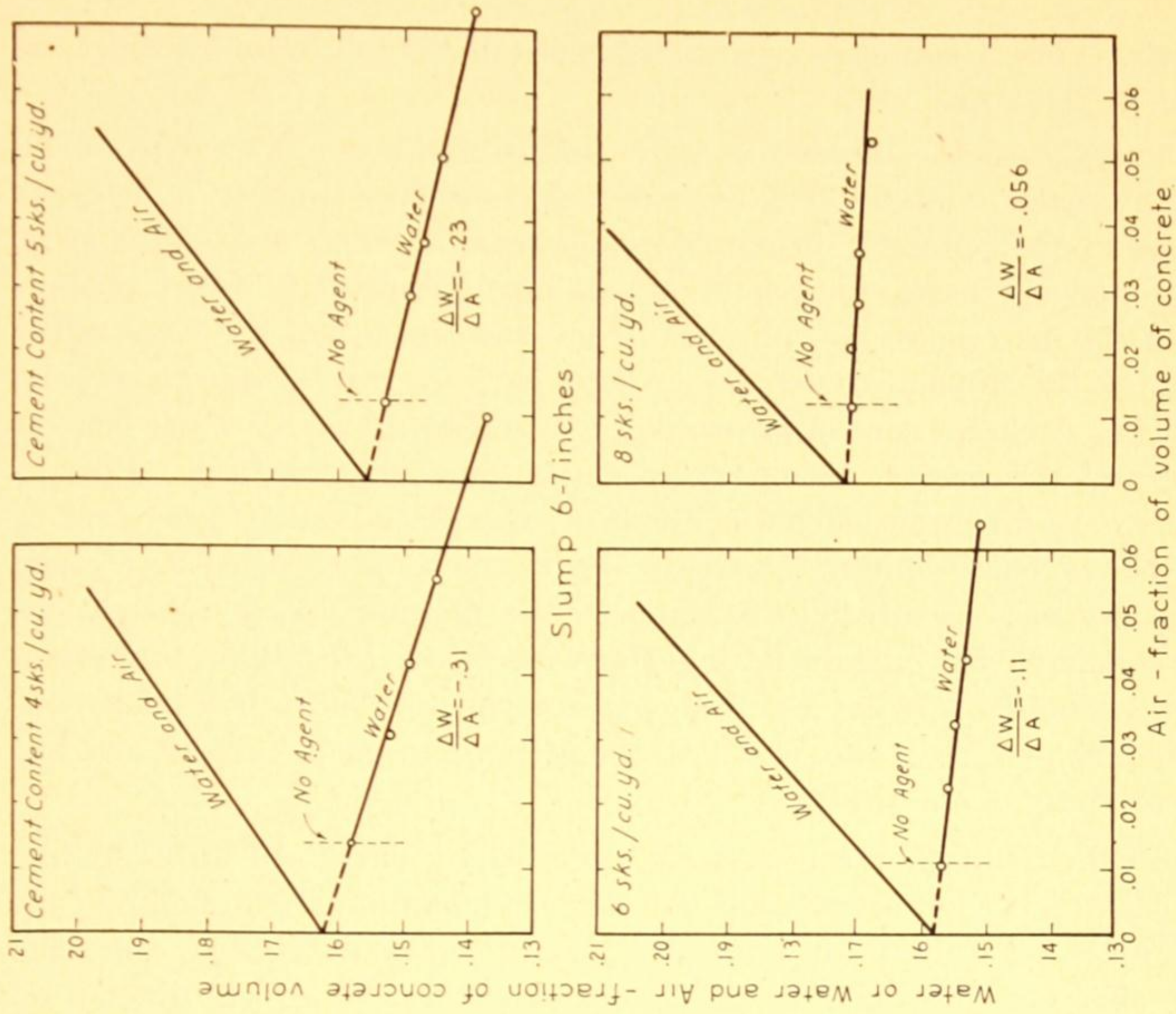


Fig. 3—Effect of an air-entraining agent on water-requirement  
Cement: a mixture of four, Type I commercial cements.

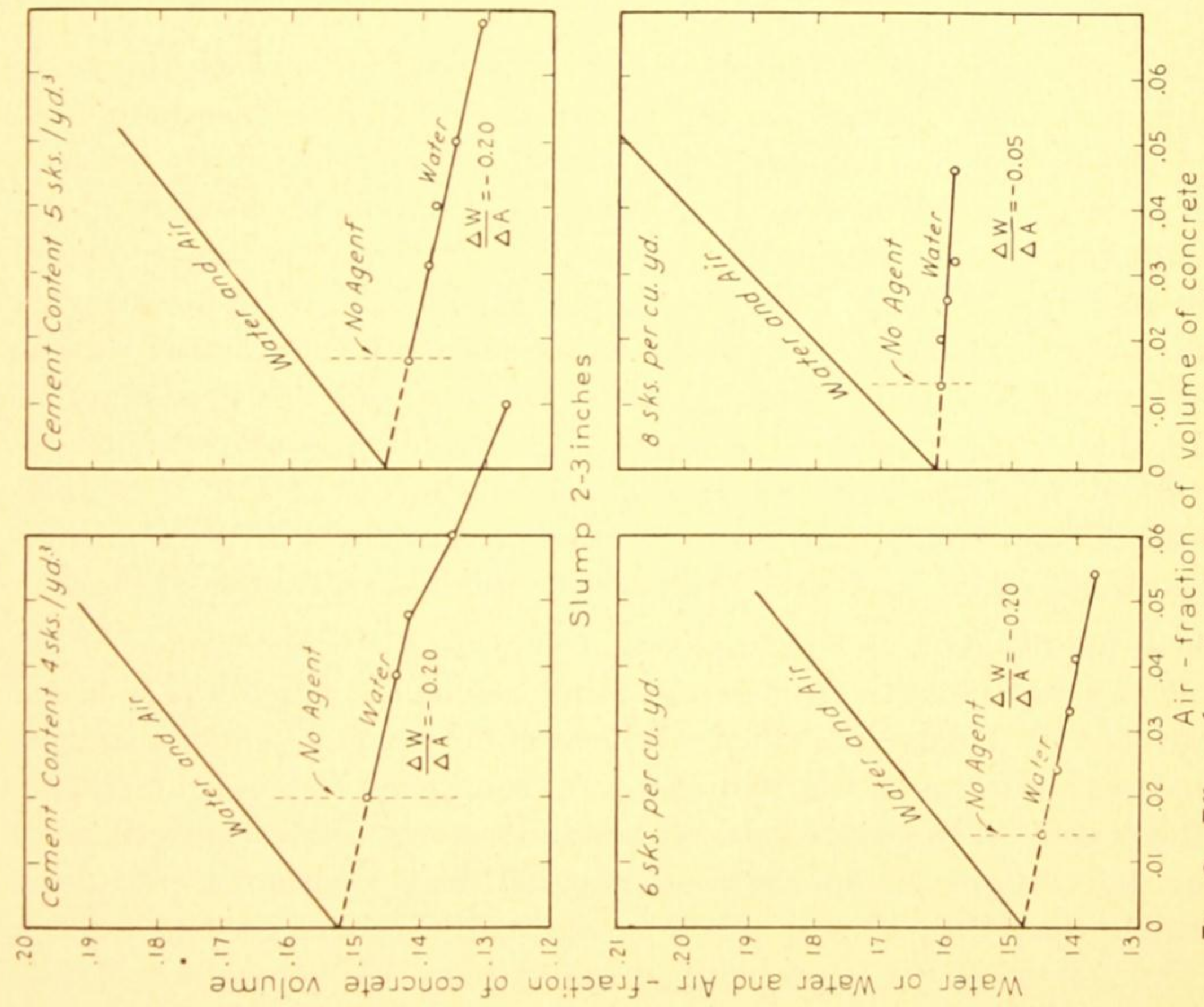


Fig. 4—Effect of an air-entraining agent on water-requirement  
Aggregate: Elgin sand and gravel, max. size 1 in.



content. Figs. 3 and 4 represent concretes of different consistencies, as stated in the titles.

In every case the increase in air content was accompanied by a decrease in water content, the decrease being directly proportional to the increase in air content. But since the decrease in water was not as great as the increase in air, the paste content also increased in direct proportion to the increase in air content. If air and water had the same effect on slump, the slope of the water curve in each diagram would have been  $-1.0$ ; i.e., each per cent of air would have replaced exactly 1 per cent of water and the paste content would have remained constant. But, as shown in the diagrams, each 1 per cent of air replaced only 0.3 per cent or less, and the paste content increased. Since the paste required for a given slump increases in direct proportion to the increase in air content, we must conclude that entrained air stiffens the paste. It follows that when the water content is not reduced, the increase in slump caused by entraining air in a given mix is due to the increase in paste content and not to a softening of the paste.

The conclusion that the paste is stiffened by entrained air is in line with the observed effect of whipping air into cream, or the stiffening that is produced when liquid-liquid emulsions are formed. Indeed, the stiffening effect of entrained air on cement paste was observed directly by Kennedy.<sup>14</sup>

Some idea as to the degree to which entrained air stiffens the paste was deduced from the data in Fig. 3. As a first step in this deduction, Fig. 5 was prepared. The lower diagram shows the relationship between water or water + air content and the cement content for mixes containing definite amounts of air, the curves being obtained by interpolation in the diagrams of Fig. 3. The positions of the lines in the upper diagram in Fig. 5 were then obtained from the lower diagram by adding the volume of the cement to that of water + air. The next step was to assume, as before, that at equal paste volumes and equal concrete slumps the pastes must have the same consistency, and then, by means of Fig. 5, to compare the composition of pastes of the same consistency with and without entrained air. The results for two paste contents are given in Table 4.

These figures show, for example, that a paste for which  $w/c = 0.583$  and  $air/c = 0.12$  had the same consistency as one for which  $w/c = 0.447$  and  $air/c = 0$ . Thus, introducing 0.12 cc of air per g of cement stiffened the paste as much as would reducing  $w/c$  from 0.583 to 0.447, i.e., reducing the water 0.136 cc per g of cement. It is not likely that pastes of these compositions would show exactly the same consistency if tested separately from the concrete, for, as indicated by Kennedy's experiments, effectiveness of the air is probably influenced by the aggregate. Never-



TABLE 4

| Air<br>Content<br>of<br>Concrete | w/c          |      | Air + w                   | Air                       |
|----------------------------------|--------------|------|---------------------------|---------------------------|
|                                  | Abs.<br>Vol. | Wt.  | $\frac{c}{e}$<br>cc per g | $\frac{c}{e}$<br>cc per g |
| Paste = 0.25                     |              |      |                           |                           |
| 0.00                             | 1.42         | .447 | .447                      | 0                         |
| 0.01                             | 1.46         | .460 | .495                      | .035                      |
| 0.02                             | 1.54         | .485 | .555                      | .070                      |
| 0.03                             | 1.85         | .583 | .703                      | .120                      |
| Paste = 0.27                     |              |      |                           |                           |
| 0.00                             | 1.31         | .413 | .413                      | 0                         |
| 0.01                             | 1.33         | .419 | .448                      | .019                      |
| 0.02                             | 1.36         | .429 | .488                      | .059                      |
| 0.03                             | 1.38         | .434 | .531                      | .107                      |
| 0.04                             | 1.40         | .441 | .575                      | .134                      |
| 0.05                             | 1.66         | .523 | .718                      | .195                      |

theless, the data show conclusively that entrained air has a stiffening effect even though it is more fluid (i.e., it has a lower viscosity) than the water it displaces. A correct explanation of the effect would undoubtedly involve the surface tension at the numerous air-water interfaces.

Returning to Fig. 3 and 4, we may note that the point for the plain mix in each diagram falls in line with the other points. This indicates that the agent had no softening effect on the paste, that is, it did not reduce interparticle attraction. Had there been a reduction in interparticle attraction the line would have passed below the point for the plain mix.

In general it appears that the lower the cement content the greater the reduction in water requirement per unit increase in air content. This is shown as a steady trend in Fig. 4, but in Fig. 3, representing the stiffer consistency, the effect is equal in the 4-, 5-, and 6-sack mixes.

So far as workability and bleeding characteristics are concerned, the effect of entrained air may be regarded as highly beneficial. It increases cohesiveness, it aids in holding the aggregate from settling while the concrete is being transported, and the increase in paste volume increases the capacity for plastic deformation.

Entrained air reduces strength, but greatly increases resistance to frost action.<sup>16</sup>

#### Effect of an agent that both reduces interparticle attraction and entrains air—Agent C

The effect of an agent of this type on water requirement and air content is shown in Fig. 6. The data are fewer than might be desired,\* but

\*Although many tests have been made on various agents in this laboratory, only a few have included several proportions of a given agent.



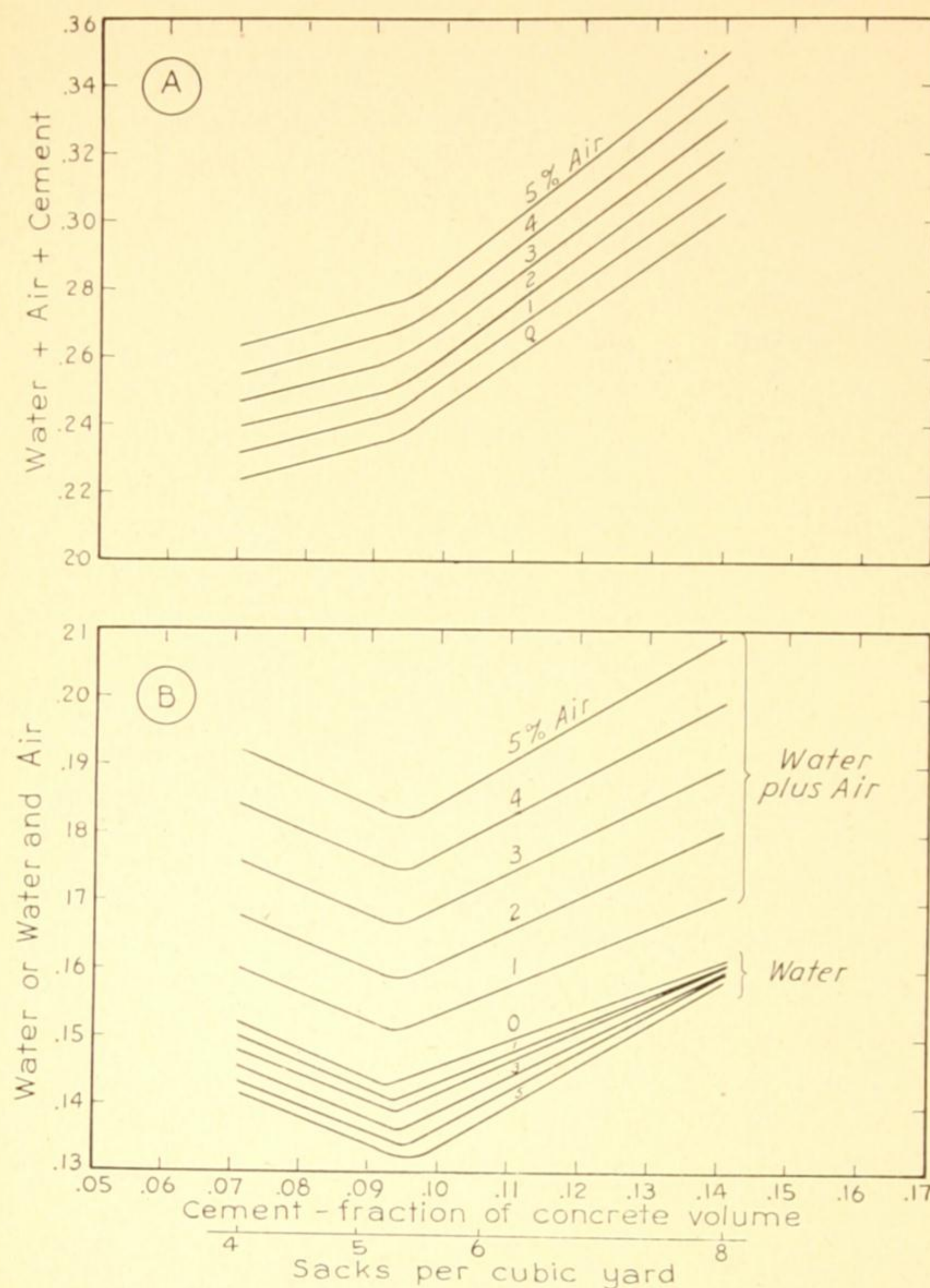


Fig. 5—Effect of an air-entraining agent on water, air, and paste content—slump 2-3 in.

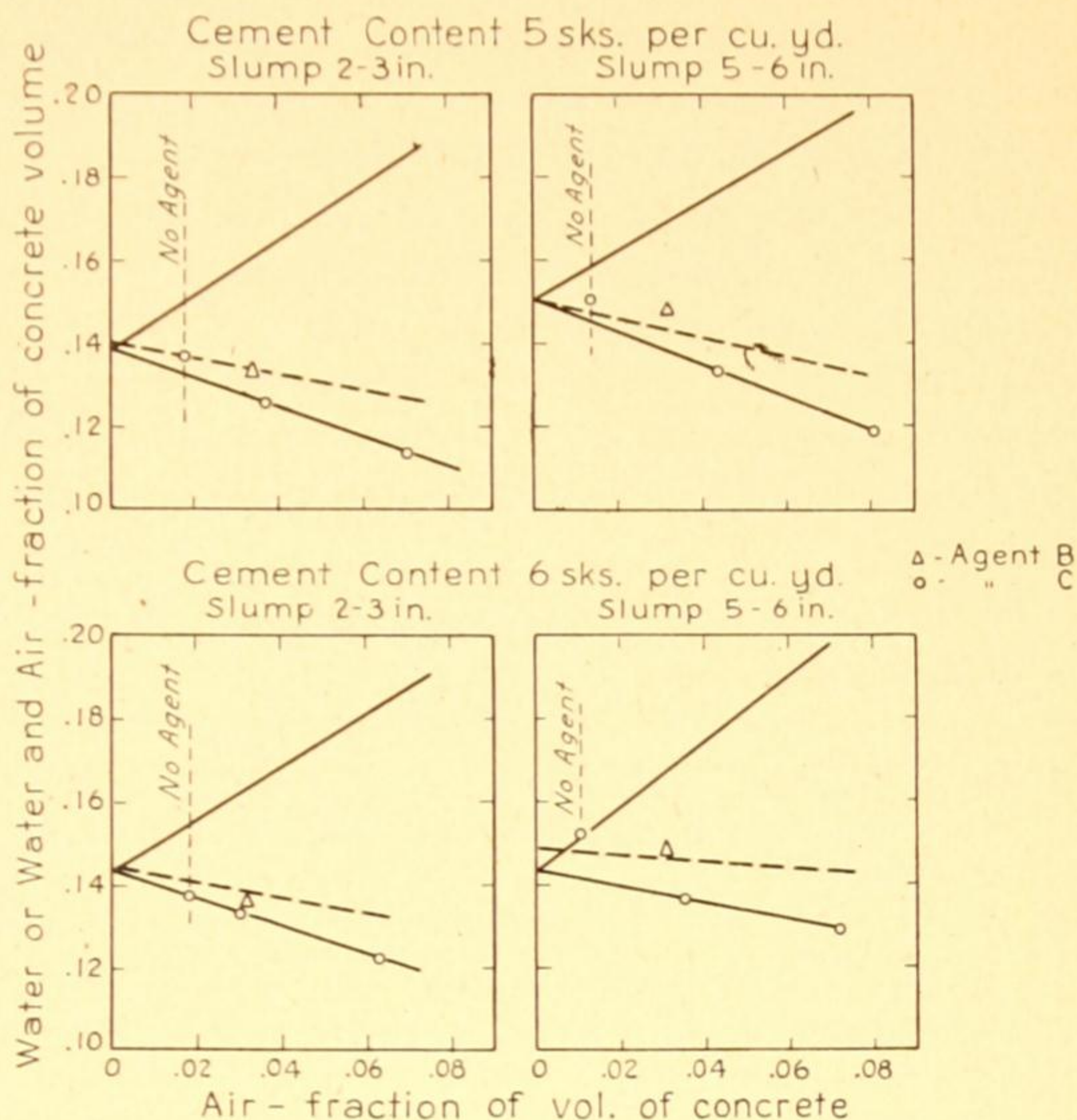
their indications are such as would be expected from the discussion of the two other types presented above. In Fig. 6 the solid lines represent the water contents and water + air contents as in Fig. 3 and 4. The broken line is drawn to have the same slope as the lines in Fig. 3 or 4, for corresponding slumps and cement contents, and to pass through the point representing the plain mix, except where adjustments were made to compensate for inequalities in slump. Thus the broken line represents the effect of an air-entraining agent, Agent B, and the solid lines, the effect of the agent which both reduces interparticle attraction and entrains air, Agent C. The triangular point in each diagram represents the one mix of each kind in this series that was made with Agent B.

Although the four diagrams are not wholly consistent with each other in all respects, they show that Agent C reduced the water requirement more than did Agent B. Presumably, this is the effect of a reduction in



**Fig. 6—Effect of an agent that entrains air and reduces interparticle attraction.**

Cement: a mixture of four Type I commercial cements. Aggregate: Elgin sand and gravel, max. size  $1\frac{1}{2}$  in.



interparticle attraction caused by Agent C, as indicated by points for the plain mixes falling above the line for Agent C.

It is clear, however, that even if Agent C did reduce the interparticle attraction, the net effect of this and the air entrainment was a stiffening of the paste. This is shown by the fact that with Agent C, as with Agent B, the paste content required for a given slump increased in direct proportion to the increase in air content. In view of this, it may be concluded that whatever undesirable effects on plasticity and bleeding characteristics the reduction in interparticle attraction might have, they are offset by the effect of the entrained air.

On the whole, it appears that *with respect to the properties of fresh concrete*, agents like B and C are beneficial, C being somewhat more so, for with an agent of this type, concrete of a given slump and air content can be obtained with less water in the concrete.

Whether or not the properties of the *hardened* concrete are benefited equally, or at all, by agents of this type is a question that cannot be dealt with in general terms. Experience indicates that some agents have no effect on the chemical processes of hardening and therefore the effects on strength can be predicted fairly well from the effect on the voids-cement ratio. Other agents, especially those that influence interparticle attraction, are liable to retard hydration and, apparently for that reason, some



are sold with an added accelerator. Agents of this type have different effects on different cements.

With respect to durability, entrained air is decidedly beneficial, and therefore the use of agents like B and C can be recommended where special protection against frost action is necessary. The beneficial effect of entrained air on durability is probably the result of providing room for expansion of water during the process of freezing.<sup>16b</sup> It is difficult to see how either dispersion, per se, or a weakening of the forces of flocculation in the absence of air entrainment, could have much influence on frost resistance.

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